

UDC 666.293.522.53

EFFECT OF THE SILICON CONTENT IN THE INITIAL ALLOY ON SYNTHESIS OF SILICON NITRIDE IN BURNING FERROSILICON IN NITROGEN

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Translated from *Steklo i Keramika*, No. 4, pp. 22 – 24, April, 2008.

Nitriding of the industrial alloy FS 65 in conditions of self-propagated high-temperature synthesis was investigated. The effect of the phase composition of the initial alloy on the combustion process was established. The dependence of the degree of nitriding of the products of combustion on the nitrogen pressure, sample diameter, and dilution of the initial batch with inert and activating additives was investigated. Silicon nitride with a 0.07% residual iron content was obtained by the method of acid concentration.

The possibility of obtaining silicon nitride by the method of self-propagated high-temperature synthesis (SHS) using industrial ferrosilicon FS 75 or the industrial powder (PUD 75) that is obtained when this alloy is ground was previously demonstrated (RF Patent No. 2257338) [1]. Calculation of the economic effectiveness of obtaining silicon nitride from ferrosilicon powder wastes (PUD 75) showed that the cost of the silicon nitride obtained is several times lower than the stabilized market price. Ferroalloy plants currently manufacture other high-silicon alloys in addition to ferrosilicon FS 75, including ferrosilicon with a 63 – 68%³ silicon content (FS 65). When FS 65 is crushed, industrial powder with a 65 – 69% silicon content is produced and must be utilized. If we consider that hundreds of tons of powdered ferrosilicon wastes are formed each year at ferroalloy plants, organization of more exhaustive processing of the wastes to obtain a valuable expensive product should be considered economically expedient.

An analysis of the published data showed that the mechanisms of combustion of FS alloy FS 65 in nitrogen have not been established. RF Patent No. 2218440 showed that the product of combustion of FS 65 in nitrogen is multiphase, with a low degree of nitriding. The product obtained (nitrided ferrosilicon) is an alloying material and can be used for manufacturing high-nitrogen steels.

The results of a study of the mechanisms of combustion of ferrosilicon FS 65 in gaseous nitrogen are reported and the

conditions of synthesis of combustion products with the maximum possible degree of nitriding are determined in the present article.

Industrial ferrosilicon FS 65 contains 66.7% silicon, and the remainder is iron and impurities (GOST 1415–93). The alloy is a two-phase material consisting of silicon and lebeautite, FeSi₂. As the phase diagram of the Fe – Si system indicates, the FeSi₂ – Si eutectic melts at 1206°C and lebeautite melts at 1220°C. On the whole, the melting point of different brands of ferrosilicon is a function of the silicon content in them. The melting point of alloy FS 65 with a 63 – 68% silicon content is 1210 – 1250°C, while it is slightly higher (1210 – 1315°C) for alloys FS 75 and FS 90 with a 74 – 80 and over 89% silicon content. The melting point of silicon is 1415°C.

The initial alloy was crushed to dispersion of less than 200 μm and poured into cylindrical tubes 40 – 60 mm in diameter with gas-permeable walls. Before synthesis, the initial ferrosilicon was dried in a vacuum drying chamber at a temperature of 150 – 200°C to eliminate moisture and volatile contaminants. The relative density of the samples was approximately 0.4. The samples were burned in a constant-pressure setup in gaseous nitrogen (99.996 vol.%, GOST 9293–74). The nitrogen pressure was varied from 1 to 10 MPa. The samples were ignited from a powdered incendiary mixture with a tungsten coil. After the combustion front passed over the sample, it was held in a nitrogen atmosphere until completely cool, the pressure was then released, and the product of SHS underwent chemical and x-ray phase analysis, as well as acid concentration to remove the iron.

The nitrogen content taken up during combustion was first determined with the gain in weight and more accurately

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³ Here and below unless specifically indicated otherwise, mass content.

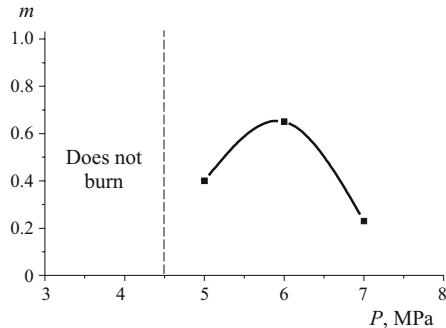


Fig. 1. Degree of nitriding m of ferrosilicon FS 65 as a function of nitrogen pressure (sample diameter of 60 mm).

in a TN-114 (LECO) instrument with the standard method, in which the hot extraction method, based on reducing melting of the analyzed samples in the medium of a chemically pure inert gas, is used.

A thermodynamic calculation was performed with Astra-4 software to estimate the maximum temperature and equilibrium composition of the combustion products [2]. The following were selected as the variable parameters: content of nitride-forming element and nitrogen pressure. The calculation showed that in nitriding of Fe–Si alloys in the 55–90% Si content range, the maximum combustion temperature is determined by the equilibrium between silicon nitride and the products of its dissociation — silicon and N_2 — and is almost independent of the silicon content in the alloy. The combustion temperature is a function of the nitrogen pressure and varies from 1930 to 2160°C when the pressure increases from 1 to 10 MPa. As a result of the analysis of the energetic possibilities of the reactions of nitriding of ferrosilicon, we found that alloys of silicon with iron can be nitrided in combustion conditions in a wide range of variation of the concentrations and pressures.

The experimental study of the effect of the nitrogen pressure on the combustion process (Fig. 1) showed that when the pressure was changed from 5 to 10 MPa, the degree of nitriding remained low, at 0.6–0.7. At a pressure of less than 5 MPa, combustion of the alloy with the indicated particle size could not be organized in the constant pressure unit. As a result of the x-ray phase analysis of samples burned at a pressure of 5 MPa and higher, it was found that silicon nitride Si_3N_4 (α - and β -modifications), the initial material ($FeSi_2$ and Si), iron monosilicide, and α -Fe were the basic phases (Fig. 2).

The low degree of nitriding of FS 65 is due to the low melting point of the initial alloy and the filtration difficulties for moving nitrogen to the reaction zone that arise due to the appearance of an iron?silicon melt. The same picture was observed in burning ferrosilicon FS 75. Due to intensive melting, the products of combustion had a low degree of nitriding and the sample burned in self-oscillating conditions. However, despite the nonstationary conditions, FS 75 burned in a wider pressure range (1–10 MPa). These important differ-

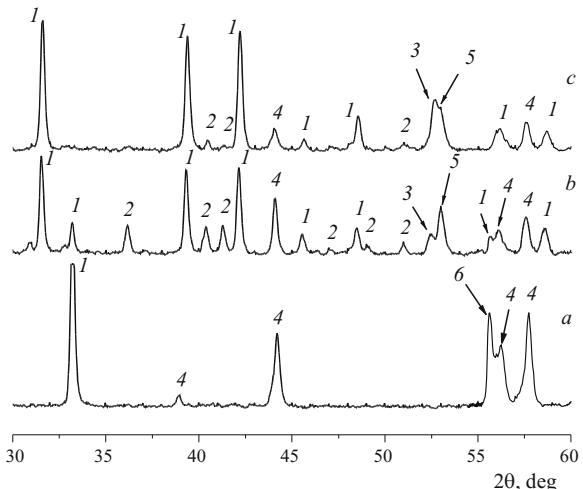


Fig. 2. Fragments of x-ray patterns of the initial ferrosilicon FS 65 (a), nitrided ferrosilicon (b), nitrided ferrosilicon in the presence of ammonium fluoride (c): 1) β - Si_3N_4 ; 2) α - Si_3N_4 ; 3) α -Fe; 4) $FeSi_2$; 5) $FeSi$; 6) Si .

ences in nitriding of the two alloys are probably determined by their phase composition.

According to the phase diagram of the Fe–Si system, the relative proportion of the primary silicon phase decreases in the order: metallurgical silicon (Si_{00} – Si_3) → FS 90 → FS 75. In the 65% alloy (FS 65), the primary silicon phase is insignificant. On the contrary, the content of lebeautite, $FeSi_2$ increases in going from FS 75 to FS 65. The secondary silicon phase (highly disperse silicon crystallizing at the eutectic point) is present in all high-silicon alloys, including alloys FS 75 and FS 65. According to the studies in [3], nitriding of ferrosilicon in the combustion conditions is a multistage process and up to 1350°C takes place due to the reaction of free silicon with nitrogen. Above 1350°C, step dissociation of iron disilicide takes place during nitriding and ends in formation of silicon nitride and α -Fe. Despite the fact that the total silicon content in the alloy is sufficient for attaining the maximum possible combustion temperature (thermodynamic calculation), its content in free form is probably insufficient for the nitriding process to occur in self-propagating conditions at nitrogen pressure below 5 MPa.

Chemical stimulation of nitriding with ammonium fluoride allowed increasing the degree of nitriding to 0.80–0.85, but the maximum degree of nitriding was not attained in the investigated range of synthesis parameters. According to the XPA results, the β -modification of silicon nitride is the basic phase (see Fig. 2c). The combustion products do not contain silicon, but there are reflections of the most stable iron silicides — the disilicide and the monosilicide, which indicates incomplete dissociation of the higher iron silicide.

The maximum degree of nitriding is attained with the complex additive NH_4F + previously nitrided ferrosilicon. The samples burned in the presence of 40–45% complex

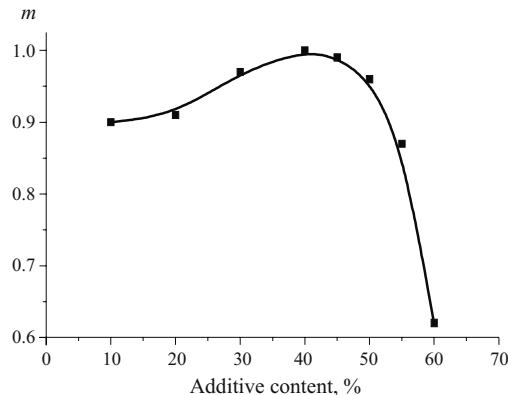


Fig. 3. Degree of nitriding m of ferrosilicon FS 65 as a function of dilution of previously nitrided ferrosilicon in the presence of 1% ammonium fluoride (50 mm sample diameter, 4 MPa pressure).

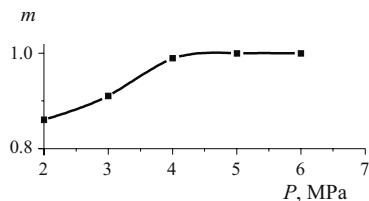


Fig. 4. Degree of nitriding m of ferrosilicon FS 65 as a function of nitrogen pressure with 40% nitrided ferrosilicon and 1% ammonium fluoride (50 mm sample diameter).

additive were homogeneous over the entire volume and were a composite material consisting of silicon nitride and α -Fe.

The studies of the dependence of the degree of nitriding of ferrosilicon with 40% dilution with nitrided ferrosilicon in the presence of 1% NH_4F on the nitrogen pressure (Fig. 3) showed that the maximum degree of nitriding is attained at a pressure of 4–6 MPa. At pressures below 4 MPa, the degree of nitriding decreases, since the rate of input of nitrogen into the reaction zone does not ensure propagation of the combustion front in self-maintained conditions (Fig. 4).

In studying the effect of the sample diameter on the degree of nitriding (Fig. 5), it was found that samples 40 and 50 mm in diameter should be used to obtain highly nitrided combustion products. When the diameter is increased to the maximum possible in the constant pressure unit (60 mm), the degree of nitriding decreases slightly, since the heat losses decrease and the role of melting processes which impede filtration of nitrogen increases.

According to the findings of the studies, a batch of combustion products, the composite $\text{Si}_3\text{N}_4 + \alpha\text{-Fe}$ was obtained (Fig. 6a). This material underwent acid concentration to remove the iron.

The results of the x-ray phase analysis indicate the absence of iron in the powder after acid concentration (Fig. 6b).

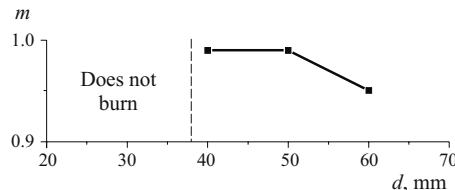


Fig. 5. Degree of nitriding m of ferrosilicon FS 65 as a function of the sample diameter for the batch (60% FS 65 + 40% Fe – Si – N) with 1% ammonium fluoride (pressure of 4 MPa).

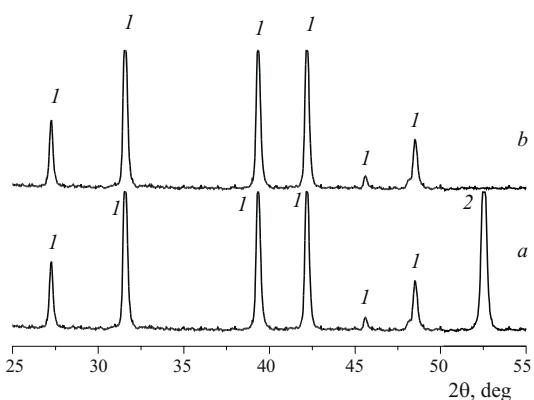


Fig. 6. Fragments of x-ray patterns of the product of combustion of ferrosilicon in nitrogen before (a) and after (b) acid concentration: 1) $\beta\text{-Si}_3\text{N}_4$; 2) $\alpha\text{-Fe}$.

The residual Fe content in the silicon nitride obtained did not exceed 0.07%.

The mechanisms of combustion of Fe – Si alloys are thus not only determined by the content of the nitride-forming element (Si) but also by the relative proportion of the primary silicon phase in the alloy. The maximum degree of nitriding is attained in incorporation of the complex additive $\text{NH}_4\text{F} +$ previously nitrided ferrosilicon in the initial alloy. The combustion products are the composite $\text{Si}_3\text{N}_4 + \alpha\text{-Fe}$. After acid concentration of the latter, silicon nitride with a low residual iron content is obtained.

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